Oxygen Reduction at Pt and $Pt_{70}Ni_{30}$ in H_2SO_4 / CH_3OH

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Introduction

The methanol crossover in the Direct Methanol Fuel Cell (DMFC) leads to a mixed potential at the cathode, resulting from the simultaneously Oxygen Reduction Reaction (ORR) and the cathodic methanol oxidation. This can be overcome by developing new electrolyte materials or /and by looking for methanol tolerant cathode catalysts. Some platinum-based alloys such as Pt-Ni, Pt-Co or Pt-Fe have already demonstrated a better catalytic activity for the ORR than pure platinum in pure acid electrolyte[1]. In this work the ORR was studied at Pt and Pt alloyed foils with 30 atom % Ni in 1 M H_2SO_4 and in 1 M H_2SO_4 / 0.5 M CH_3OH by means of Rotating Disc Electrode (RDE).

Results

Figure 1. shows cyclic voltammograms (CV´s) of Pt and $Pt_{70}Ni_{30}$ in 1M H_2SO_4. The hydrogen adsorption and desorption peaks are more pronounced at pure Pt that at $Pt_{70}Ni_{30}$. Both electrodes have similar roughness factors closed to 1.9. XPS analysis have shown a Pt enrichment at the alloy electrode surface after the experiments[1,2].

The methanol oxidation, in absence of oxygen in the electrolyte, at Pt and $Pt_{70}Ni_{30}$ in 1 M H_2SO_4 / 0,5 M CH_3OH is pictured in figure 2. The peaks Ia and Ib at ca. 700 mV vs. Ag/AgCl represent the anodic methanol oxidation at Pt and $Pt_{70}Ni_{30}$, respectively. In the negative going potential scan, a "further" methanol oxidation can be observed at Pt and $Pt_{70}Ni_{30}$ as well (peaks IIa & IIb, respectively).

Figure 3 summarizes some ORR measurements in pure H_2SO_4 and in methanol containing H_2SO_4, which were carried out at with the RDE. $Pt_{70}Ni_{30}$ shows a better activity for the ORR than Pt in pure acid solution (curves a and b, respectively). In presence of methanol, the alloy exhibits a higher selectivity for the ORR than pure Pt (curves bb and aa, respectively).

Conclusion

In pure sulphuric acid, $Pt_{70}Ni_{30}$ has exhibited about 80 mV less overpotential at 1 mA cm^{-2} than pure Pt for ORR. In methanol containing electrolyte solution $Pt_{70}Ni_{30}$ has a 11 times higher limiting current density than Pt. One explanation could be the higher exchange current density for the ORR observed at the Pt alloy. During all the measurements, no significant electrochemical activity loss was observed for the ORR at $Pt_{0.7}Ni_{0.3}$. In this way, a more methanol tolerant cathode catalyst for DMFC could be applied.

References

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in preparation.

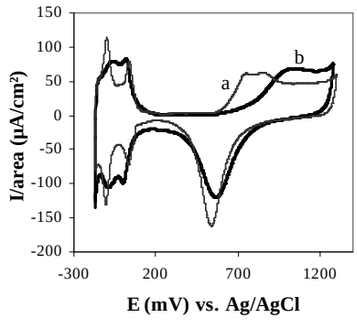
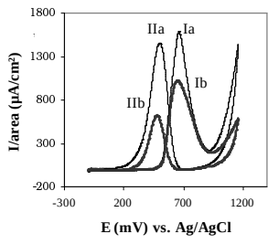


Figure1: CV´s of Pt (**a**) and $Pt_{70}Ni_{30}$ (**b**) in 1M H_2SO_4 at $dVdt^{-1}$=40 mV s^{-1}



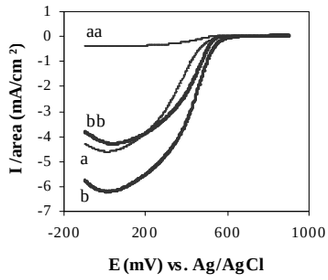


Figure 2: CV´s of Pt(**a**) and $Pt_{70}Ni_{30}$ (**b**) in 1 M H_2SO_4 / 0,5 M CH_3OH at $dVdt^{-1}$=40 mVs^{-1}

Figure 3: ORR at Pt(**a**) and $Pt_{70}Ni_{30}$ (**b**) in 1 M H_2SO_4 (**a**, **b**) and in 1 M H_2SO_4 / 0,5 M CH_3OH (**aa**, **bb**), at $dVdt^{-1}$=5 mVs^{-1}, 3000 rpm and at room temperature